

Studies of Nanoparticles Assemblies at Fluid Interfaces

Y. Lin, A. Böker, H. Skaff, D. Cookson, P. Thiyagarajan, Q. Wang, A. D. Dinsmore, T. Emrick, T. P. Russell

Directed self-assembly of nanoparticles opens new avenues of technology through the controlled fabrication of nanoscopic materials with unique properties. Ligand-stabilized colloidal nanoparticles are ideally suited to hierarchical self-assembly, because the nanoparticle core dictates optical, electronic, or magnetic properties, whereas the surface-bound ligands define the particle's interactions with its surroundings. A fluid-fluid interface offers potential for such assembly and for the chemical manipulation of nanoparticles. The self-assembly of particles at fluid interfaces, driven by the reduction in interfacial energy, is well established. For nanoparticles, however, thermal energy, which causes spatial fluctuations of the particles, is comparable to the interfacial energy. This energy balance results in a weak interfacial segregation of nanoparticles that open avenues to a size-selective particle assembly, and two-dimensional phase behavior. The detailed structure of the nanoparticle assembly was studied using electron microscopy, atomic-force microscopy, and x-ray scattering *in-situ*, which indicate that the particles form a densely packed monolayer. The dynamics of the nanoparticles at the fluid interface, probed using fluorescence photobleaching methods, suggest a liquid-like behavior.

For optimal utilization of nanoparticles at fluid interfaces, methods are needed to provide robust assemblies so that the interface can be removed after the assembly. Here we describe chemical cross-linking of the ligands attached to the nanoparticles as an effective route to this end. The ability to functionalize the ligands and provide rapid diffusion of reagents to the fluid/fluid interface allows stabilization of the nanoparticle assemblies via cross-linking to give nanoparticles embedded in a network of crosslinked ligands. These composite organic-inorganic, nanometer-thick membranes prevent convection but allow diffusion of small molecules across the interface. Interfacial crosslinking at droplet surfaces enables the encapsulation of water-soluble or oil-soluble

materials inside the resulting nanocontainers. By varying the concentration of reactive moieties, it will be possible to control the permeability and strength of these nanostructured membranes.

More recently, the assembly of virus and other biological complexes at fluid interfaces was studied. Viruses and other bioparticles are both important biological entities and chemical assemblies with unique structure and functional diversity. Again, interfacial assembly renders an easy route to direct and assemble the bioparticles into 2-D or 3-D constructs, with hierarchical ordering. These enable the potential use of bioparticles as a natural supramolecular building block to obtain materials with well-defined specific bio-functionalities.

Reference:

1. Lin, Y., Skaff, H., Emrick, T., Dinsmore, A. D. & Russell, T. P. Nanoparticle assembly and transport at liquid-liquid interfaces. *Science* **299**, 226-229 (2003).
2. Lin, Y., Skaff, H., Böker, A., Dinsmore, A. D., Emrick, T. & Russell, T. P. Ultrathin cross-linked nanoparticle membranes. *Journal of the American Chemical Society* **125**, 12690-12691 (2003).
3. Böker, A., Lin, Y. et al. Hierarchical nanoparticle assemblies formed by decorating breath figures. *Nature Materials* **3**, 302-306 (2004).
4. Lin, Y., Böker, A., Skaff, H., Cookson, D., Dinsmore, A. D., Emrick, T. & Russell, T. P. Nanoparticle assembly at fluid interfaces: structure and dynamics. Manuscript submitted to *Langmuir*.